

PROCEDURES FOR PETROPHYSICAL, MINERALOGICAL AND  
GEOCHEMICAL CHARACTERIZATION OF FINE-GRAINED  
CLASTIC ROCKS AND SEDIMENTS

August 1979

by

Edward B. Nuhfer  
J. A. Florence  
J. L. Clagett  
J. J. Renton  
R. R. Romanosky

Prepared for the United States Department of Energy  
Morgantown Energy Technology Center  
Morgantown, West Virginia

by

West Virginia Geological and Economic Survey  
Morgantown, West Virginia

under

Contract EY-76-C-05-5199

## CONTENTS

Abstract .....	1
Introduction .....	3

### Procedures Arranged in Order of Performance

Initial Cutting of Core - Preparation of Radiography Slabs J.A. Florence .....	5
---	---

Subsampling of Core and Apportionment of Sample for Petrographic, Petrophysical, and Geochemical Analyses J.L. Clagett .....	7
--	---

Preparation of Ground Samples for XRD, XRF, and Matrix-density Analysis J.J. Renton .....	9
---	---

Determination of Density and Porosity E.B. Nuhfer .....	11
--	----

Preparation of Membrane-filter Mounts for X-ray Diffraction E.B. Nuhfer .....	24
--	----

Chemical Analysis of Fine-grained Clastics using $\text{LiBO}_2$ - $\text{HCl}$ - $\text{HF}$ Dissolutions E.B. Nuhfer and R.R. Romanosky .....	30
---	----

PROCEDURES FOR PETROPHYSICAL, MINERALOGICAL AND  
GEOCHEMICAL CHARACTERIZATION OF FINE-GRAINED CLASTIC ROCKS  
AND SEDIMENTS

Edward B. Nuhfer<sup>1</sup>, J. A. Florence<sup>1</sup>, J. L. Clagett<sup>1</sup>, J. J. Renton<sup>1</sup> and R. R. Romanosky<sup>1</sup>  
by

ABSTRACT

These methods result from about four years of study of shales and recent fine-grained muds. Characterization of shales has been a topic of intensive research under the Eastern Gas Shales Project through a contract study to West Virginia Geological and Economic Survey funded by United States Department of Energy.

The geological record locked within sedimentary rocks has usually proven best interpreted after study of modern equivalent analogues. The study of contemporary delta and shallow marine environments has led to a reasonably good understanding of depositional models of sandstones; likewise, the study of contemporary reefs and shallow marine shelf environments has led to a wealth of information concerning carbonate diagenesis and stratigraphy. However, the study of shales is not nearly so well supported through study of modern equivalent analogues where fine-grained muds are presently deposited. Thus, a set of suggested analytical procedures should be applicable to both shales and fine-grained muds. Such sediments do not lend themselves particularly well to characterization by conventional petrographic methods. Problems in shales arise because the grain sizes in these rocks prevent mineralogical characterization by the petrographic microscope. In addition, their high content of organic matter, of sulfur, their fragile mechanical properties, their heterogeneity and their tendency to swell, crack, and chemically react with even atmospheric humidity causes problems to the petrologist and geochemist. Modern muds cause much the same problem, and the study of fine-grained sediments in true suspension presents the additional obstacle of small amounts of available sample which is often irreplaceable. Heterogeneity requires that large numbers of samples be analyzed to generate a sufficient sample base from which conclusions may be made. Many analytical procedures used conventionally are too tedious to be realistically applied to large numbers of sample. All methods given in this text are suitable for rapidly processing large numbers of samples cheaply and quickly with very good precision.

The procedures which follow have been proven in the detailed characterization of over 600 shale samples and 500 samples of recent suspended lacustrine sediments. Density and porosity measurements sufficient to provide good between-sample comparisons of shales with only about 1 or 2% porosity are possible using equipment found in most laboratories providing that attention is given to sources of small errors and suitable immersion fluids are used. Mineralogical composition can be precisely characterized by X-ray diffraction, providing that a careful sample preparation scheme is adhered to. Such precision can be maintained on samples as small as 20mg in size. Elemental analyses are better performed on high-temperature ash remaining after

---

<sup>1</sup>West Virginia Geological and Economic Survey

loss-on-ignition than on original whole sample. Complete chemical analyses of major, minor, and many trace elements can be obtained on sample sizes as small as 20mg of ash. Precision afforded by mineralogical and chemical methodology is sufficient to allow merging of data from these two sources for statistical analyses. Presence of significant amounts of X-ray-amorphous mineraloids is now thoroughly documented in recent muds and is possibly present in many shales. This material complicates the problem of merging mineralogical and chemical data in statistical studies. However, when a sufficiently large sample base is developed, meaningful interpretation can be made from lack of expected statistical trends as well as by those confirmed which are previously suspected.

## INTRODUCTION

The volume of research on fine-grained sediments represents a minority of the published literature of clastic rocks. Therefore, most laboratory methodology used for study of sedimentary rocks is designed for use with coarse-grained clastics and carbonate rocks. Such standard procedures fail to produce the desired information from specimens of shale or fine-grained muds. Most petrographic studies are based upon features easily measured or described through use of the polarizing microscope. These are performed on rocks where the grain size of the constituent components roughly equals or exceeds the thickness of a standard thin section (about 20 to 30 microns) and thus optical petrography texts and references are geared toward description of mineral properties which manifest in grain sizes through the silt and sand sized particles.

Particles in the very-fine silt and clay sized ranges lack the properties of birefringence and pleochroism that are common properties used to identify and characterize minerals in coarser sediments. Moreover, the superposition of minerals in micron-sized grains one over the other in a 20 micron-thick thin section renders impossible any meaningful quantitative results from point-counting of grains in thin-section.

Contrary to statements in many introductory geology textbooks, porosity values in shales are extremely low, averaging about perhaps 2% after lithification. Such final porosities result from the compaction of initially flocculent muds with porosities over 90%. To compare porosity among rocks which possess perhaps a total range of porosity of only two or three percent requires very precise and accurate measurement, more so than is generally required for most reservoir rocks with porosity ranges of perhaps thirty or forty percent.

Studies of suspended sediments present all of the above problems plus the added problem that collection of the amounts of sample that are required for analyses is accomplished only through laborious filtration of large amounts of sample or long term accumulation of sample in sediment traps.

Development of methods for characterization of fine-grained sediments came from two main sources; the Eastern Gas Shales Contract EY -76-C-05-5199 to West Virginia Geological Survey from U.S. Dept. of Energy, and the doctoral research of Edward Nuhfer which involved analysis of sediment-trap samples. This latter study was supported by West Virginia Geological Survey and the above contract through use of laboratory facilities.

Both of the above studies required detailed characterization of fine-grained sediments, and many of the procedures which were developed earlier in the sediment-trap studies were immediately adapted by the Survey laboratories for the characterization of shales and other fine-grained clastics such as coal ash, peats, and recent muds. Specifically, the density-porosity method, the membrane-filter mount for X-ray diffraction and the rapid flux-fusion method for whole-rock analysis were developed by Nuhfer in his doctoral research, and later improved during the contracted shale characterization tasks. The methods of slabbing of core for X-radiographs and of subsampling so as to provide correlative samples were developed directly on the Eastern Gas Shales Project.

The additional methods of fabric analysis utilizing the X-radiographs and direct print imaging of thin-sections have already been described elsewhere (Nuhfer and Vinopal, 1979a;b) and thus are not repeated herein. The reader is also referred to Nuhfer (1978), Nuhfer and Romanosky (1979), and Nuhfer and Renton (1979) for additional information on applications of the methodology contained herein.

The combining of X-ray fluorescence elemental analyses with X-ray diffraction analyses to produce improved estimates of absolute mineral composition of shales has been submitted by J.J. Renton under separate cover and thus only the sample preparation procedures for X-ray fluorescence and X-ray diffraction are given here but these are sufficient to permit the reader to perform and duplicate the type of analyses performed by us on the Eastern Gas Shales Project.

#### REFERENCES CITED

- Nuhfer, E.B., 1978, Methods for petrological and geochemical characterization of sediment trap samples: unpublished manuscript as Appendix B of Temporal Variations in Lacustrine Sediments as Determined from Automated Sampling, 1979, PhD thesis, Univ. New Mexico, Copyright E.B. Nuhfer, 45p.
- Nuhfer, E.B., and Renton, J.J., 1979, Whole-rock vs. whole-ash analysis of sedimentary rocks - the elusive 100% summation: Atomic Absorption Newsletter, in review.
- Nuhfer, E.B., and Romanosky, R.R., 1979, Determination of lead in earth materials from lithium metaborate flux-fusion dissolutions: Atomic Abs. Newsletter, v.18, n.1, p.8-9.
- Nuhfer, E.B., and Vinopal, R.J., 1979a, Applications of direct-print imaging of thin-sections: Jour. Geological Ed., v.27, p.64-66.
- Nuhfer, E.B., and Vinopal, R.J., 1979b, X-radiograph atlas of lithotypes and other structures in the Devonian shale sequence of West Virginia and Virginia: N.T.I.S., in review.

## INITIAL CUTTING OF CORE

### PREPARATION OF RADIOGRAPHY SLABS

James A. Florence

This phase begins after complete macroscopic description of the core and fractographic logging have been performed and samples have been taken by the petrologist. Many of the samples selected for examination are found to be fractured as a result of core extraction and handling. Because of fragmentation, it is advisable that tape be liberally utilized to hold the sample together at time of collection. Epoxy glue is used to reconstruct the core so that sufficiently large lengths of the rock can be exposed during the slabbing procedure to reveal representative geologic features.

After this process, core sections are marked with a carborundum-tipped scribe as to orientation (E, W, N, S) and depth to the top of each core section. Multiple labelling is needed because in the cutting process some flakes and pieces may be lost. All sections are longitudinally cut through the diameter along the north-south plane, this being chosen for uniform between-sample comparison.

After the first longitudinal cut has been made of the core section, the final slab of the radiograph is produced by advancing the carriage (a constant number of turns of the advancing screw each time) to achieve a standard two-millimeter slab from each sample. This is required to achieve uniform optimum radiographic exposure times. The highly brittle and easily fractured nature of shales (and also coals) require employment of a backing material prior to cutting the slab. The procedure is as follows: after the first cut, the half-core retained in the carriage is wiped of cutting mud and blade coolant (kerosene). The core half is then flooded with acetone and cleaned again. Finally, the cut face is again flooded with acetone and a sheet of cellulose acetate is rolled onto the vertical core half from the bottom to the top. The core half with backing applied is then allowed to air dry for a few moments - and then the slab is sawed to 2 mm thickness (Figure 1).

After the slab has been cut, it is retrieved from the saw and washed of the cutting mud and blade coolant in a basin of warm soapy water and then rinsed in warm water. Backing material can be removed at any time, but for ease of handling it is usually left attached until just prior to radiographing.

At the end of the slabbing procedure, one of the half-core sections is cleaned, dried and the cut face is ground with a flat-

faced electric sander to remove any marks. Labels are checked for clarity and permanence. Finally, this half-core is sprayed with three light coats of plastic lacquer (Krylon) to protect the core from degradation in the atmosphere. The coated half-core constitutes the archive sample.

The remaining half-core is then cleaned, dried, and a selected area of the face is marked for thin-sectioning with a piece of Scotch Magic Tape about 1" long. Tape is also applied to the correlative area of the archive sample to show which portion of the core served as sample source.

The procedures for making radiographs of shales and coals are described respectively by Renton (1977) and Vinopal (1979). The employment of radiographs for classification of fine-grained rocks as fabric-element-based lithotypes is detailed by Nuhfer and others, (1979). Classification by lithotype is valuable for gaining information on both productive potential and depositional environments. Further characterization by physical testing and compositional analysis is made much more valuable when the tests can be related back to specific rock fabrics and thus lithotype classification should precede performance of any destructive testing (Nuhfer, 1979, personal communication).

#### References Cited

- Nuhfer, E.B., Vinopal, R.J., and Klanderman, D.S., 1979, X-radiograph atlas of lithotypes and other structures from the Devonian shale sequence of West Virginia and Virginia: N.T.I.S., Morgantown Energy Technology Center, in review.
- Renton, J.J., 1977, Some practical considerations in X-radiography: N.T.I.S., MERC/SP/77-7, 27p.
- Vinopal, R.J., 1979, X-ray radiography of coal: Jour. Sed. Petrol., v. 48, in press.



SUBSAMPLING OF CORE AND APPORTIONMENT OF SAMPLE  
FOR PETROGRAPHIC, PETROPHYSICAL,  
AND GEOCHEMICAL ANALYSES

J. L. Clagett

Because a large number of analytical measurements are made on a single labeled sample, it is imperative that subsamples used for each measurement come from the same representative portion of the core. Vertical variations in density and composition occur even over small distances less than a centimeter. Horizontal variations also occur, but are generally less abrupt and of smaller magnitude. Consequently, uniformity is optimized by confining each subsample of a sample to the same vertical interval (Fig. 1).

After a slab saw has been utilized to isolate the interval previously marked with Scotch Magic Tape in a block, two vertical cuts provide subdivisions "a" through "c". Part "a" is utilized for petrographic thin sections. Consequently, it must be labeled with an arrow to denote vertical orientation of the specimen as well as the sample number. Part "b" is ground as described by Renton in this methodology report. The ground sample is subsequently used for X-ray diffraction studies, chemical analyses, matrix-density determinations, and loss-on-ignition tests. Part "c" is used for bulk-density determination.

Most thin sections utilized in our petrographic study of shales are prepared by an outside firm. On those sections we have made in house, we find that progressive grinding from #240 through #1000 grit, followed by polishing with magnesium oxide or aluminum oxide metallographic compound on both the side of the block glued against the glass slide and the upper face of the final section, provides an excellent specimen for observation in either reflected or transmitted light.

Freshly trimmed and polished blanks should be dried in an oven at low temperature (40°C maximum) for a day to remove any residual moisture which might prevent a good bond when the blank is affixed to the glass slide. Commercial petrographic slides, even those labeled as "pre-cleaned" are generally dirty and require cleaning with methanol and lens tissue to insure a good bond. Non-clouding epoxy such as Armstrong 271 is recommended for mounting blanks onto glass slides.

After grinding and polishing, the sections are stained with Alizarin Red S dissolved in 2% HCL for positive identification of calcite. After thirty seconds the slide is rinsed with distilled

water from a wash bottle and immediately blown dry with compressed air.

Cover slips are cleaned with lens tissue then affixed onto the thin section with either a solution of Canada balsam in toluene or a commercial agent such as "Liquid Cover Slip". The cover-slip cement requires curing on a flat, level surface to maintain a good bond.

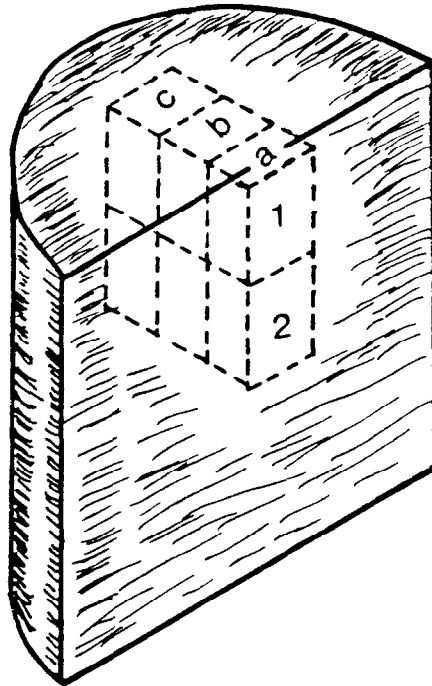


Figure 1. Schematic showing apportioning of core for subsampling. From 1 is taken "a" for thin section, "b" for source of ground sample for matrix density, X-ray diffraction, and chemical analyses, and "c" for source of bulk density. Back-up sample "2" is substitute for 1 in event of complete loss or destruction of any subsample. Face of entire core-half is thin-slabbed for radiography prior to cutting out of "1" and "2". Other half of core is coated with Krylon and saved as an archive.

## PREPARATION OF GROUND SAMPLES FOR XRD, XRF,

### AND MATRIX-DENSITY ANALYSIS

J. J. Renton

The samples are first crushed by hand in a steel mortar and pestle. The crushed sample is then further reduced by grinding in a Spex Mixer-Mill using the 30 ml tool steel grinding vial with the cap-compression type closure.

The grinding vial is filled approximately 1/3 full with the crushed sample. Three hundred 1/8" stainless steel balls and 20 ml of methanol are added to the vial which is then sealed. Shale samples are ground for 15 minutes.

Upon completion of the grinding, the resultant slurry is poured into a ceramic evaporating dish through a fine wire mesh screen to remove the steel balls. The interior of the vial, the cap, and the steel balls are then thoroughly flushed with methanol into the evaporating dish. The slurry is allowed to evaporate to dryness at room temperature. The dried sample cake is hand pulverized, and the ground sample is retained in air-tight vials until utilized for analysis. This ground sample is utilized for XRD, matrix-density determinations, sulfur analyses, and loss-on-ignition determinations.

Samples are prepared for XRF analysis by pelletizing. Five grams of sample (one spex-cap full) are weighed to the nearest milligram. Chemplex Industries X-ray-mix is then added into the sample to equal ( $\pm 1$  mg) 10% of the weight of the sample. The sample/X-ray mixture is then tumble blended for 2 hours. Upon completion of the initial blending, the sample/X-ray-mix blend is further ground and homogenized in a Spex Shatterbox for 3 minutes.

After blending and grinding, the sample/X-ray-mix blend is pelletized. A Spex 33 mm evacuable die is prepared by assembling the die base, die body, and lower platen. The sample/X-ray-mix blend is poured into the die. The die ram is slowly lowered into the die and rotated in order to spread the sample/X-ray-mix blend uniformly over the lower platen surface. The ram is then carefully removed so as not to disturb the compacted mixture. The upper platen is then lowered into place, followed by the ram, and the mixture is pelletized under a 15 ton total load maintained for 2 minutes. The pressure is released, the die is rotated 180°, and the pellet is then removed for analysis.

In this research, calibration curves for the X-ray fluorescent analyses were built from 12 secondary standards. These curves were obtained by atomic absorption and colorimetric methods via the flux-fusion scheme of Nuhfer and Romansky given in this paper. Twelve USGS-NBS whole-rock standards were processed via the same flux-fusion scheme to establish the compositions of these 12 shale standards. The secondary standards were chosen on the basis of a spread of values of loss on ignition which takes into account matrix differences caused by variable amounts of organic matter.

## DETERMINATION OF DENSITY AND POROSITY

E. B. Nuhfer

Matrix-density determinations are performed on ground samples, the same ground samples which are utilized for X-ray diffraction measurements and geochemical analyses. The theory of utilizing ground samples rests on the premise that fine grinding combined with vacuum impregnation will open virtually all of the pore space in the rock to be filled with the impregnation fluid in which the power is immersed. Error will be introduced if solid material is either added or removed during the sample-preparation procedure. If the sample is not kept cool during the grinding process, possible artificial pore volumes may be created by removal of volatile materials such as organic compounds. The choice of a coolant for the grinding process is of some importance. The research staff at this Survey chose methanol because it is not likely to be reactive with the mineral components and because its high volatility permits its rapid removal from the ground sample at room temperature.

Once the sample has been dried at room temperature, the question arises of whether or not to dry the sample further prior to performing the actual matrix-density determination. Drying at 100°C for seven days in an ordinary oven was suggested by Brownell (1977) and at over 120°C overnight in a vacuum oven (Kalyoncu and others, 1977). The rationale for oven drying is to remove extraneous water vapor possibly sorbed on the shale from atmospheric humidity. For most quantitative chemical analyses, oven drying is a standard procedure to insure a truly representative sample weight.

For measurement of shale densities, however, the objective is to compare the weight-per-unit-volume of the matrix with a weight-per-unit-volume of the bulk sample, keeping both samples as representative of actual subsurface formation as possible, in order to arrive at a representative porosity value. Available data now indicate that the Devonian shales of West Virginia were probably never heated much beyond 100°C at maximum burial and were certainly never subjected to such temperatures at atmospheric or sub-atmospheric pressures. To investigate the probability of artificial porosity being created during oven drying, several thermograms were run on Devonian shales from 60°C through 100°C and 60°C through 250°C. The removal of both water and organic matter could be documented in some samples in the low temperature range, whereas other samples lost no detectable water or organic matter through 250°C. Still other samples lost water at the lower temperatures and organic material above 100°C. Therefore oven drying may remove natural constituents of the shales in an

unpredictable and uncorrectable manner, and the removal of such constituents introduces artificial porosity. Such artificial porosities may not be significant additions in ordinary reservoir rocks where porosity values range from about 8% to 40%, but they are important errors in shales whose mean porosity appears to be less than 2.5%. Thus we do not recommend oven drying of shale specimens. Using the methods outlined in this paper, we have run replications of density measurements on the same sample on different days, and precision and accuracy have remained within the limits of analytical error.

In order to allow valid comparisons between different density-porosity measurements and with other petrologic or geochemical properties, it is essential that truly correlative samples be used for comparison. The method through which correlative samples are prepared begins in the initial cutting of the sample from the core. The samples used for these comparisons must be absolutely taken from the same horizontal section of core (see Figure 1 in discussion by Clagett in this paper).

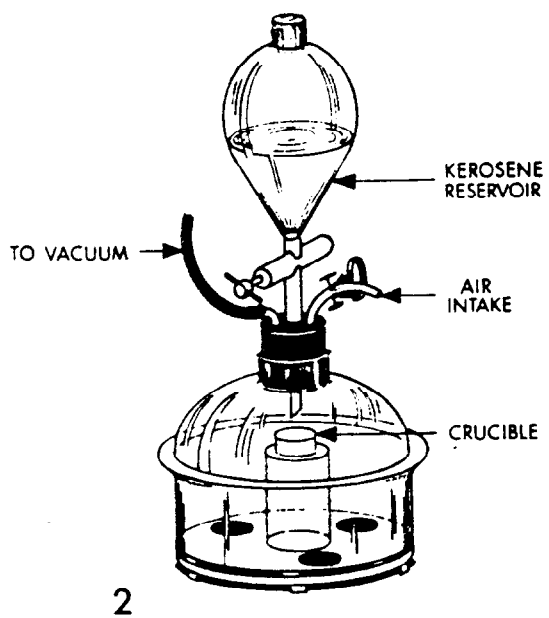
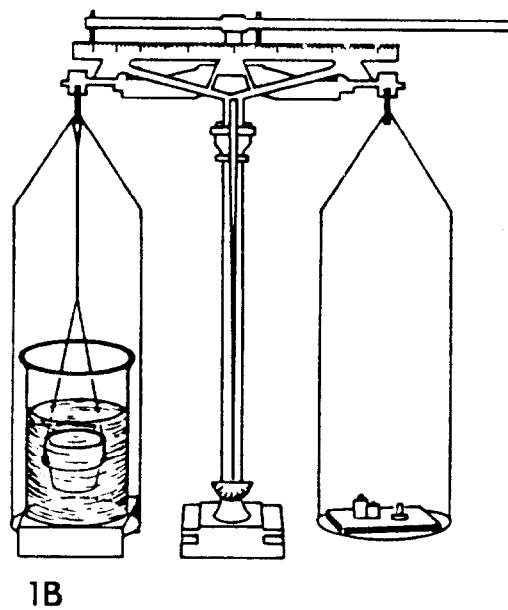
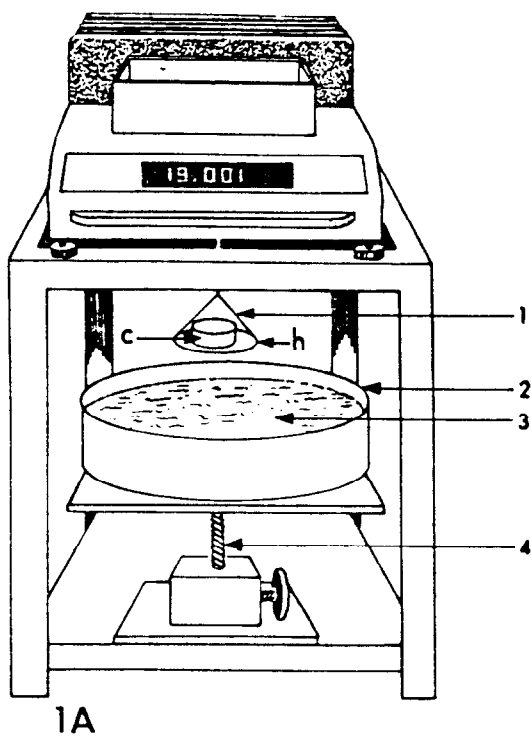
Samples taken from two vertical depths differing by as little as a centimeter have proven to have widely divergent densities. Even when the above recommended procedure is carefully adhered to, occasional heterogeneities such as a vug or a pyrite nodule in either the bulk or the grain density specimen will produce unreasonable comparisons and should be expected. Replicate runs on both density measurements will establish whether the discrepancy was created during the density-measurement process or whether it reflects an inherent characteristic of the sample.

1) vacuum-crucible method of measuring matrix density. A metal combustion crucible is placed on the sample pan hung beneath a high precision electric balance as shown in Figure 1A. The laboratory jack is subsequently raised to lock position where the crucible is completely immersed in kerosene. A piece of weigh paper is placed atop the balance pan and the balance is zeroed utilizing the automatic tare option. About two grams of dry rock powder are placed on the weigh paper and the weight of the powder to three decimal places is recorded. About one-half of the kerosene in the crucible is poured back into the wide pan and the remainder into a waste container.

The metal crucible is then gently wiped dry and the powder from the weigh paper is poured completely into the crucible. The weigh paper is returned to the balance pan. The crucible is placed in a vacuum chamber (Figure 2) which is then evacuated to capacity (we evacuate to about 0.2 mm of mercury). Only after evacuation to capacity is the kerosene from the reservoir slowly released to cover the sample in the crucible. The crucible is allowed to stand under continued vacuum for at least two minutes

Figure 1-A - Arrangement of high-precision top-loading electrical balance for determination of matrix density by vacuum crucible method. "C" is crucible; "h" is hanging underslung pan attached to balance; 1) designates thin support wires of metal or nylon; 2) designates wide reservoir pan; 3) kerosene immersion fluid; 4) laboratory jack designed with locking mechanism to allow return of reservoir to some raised position when pan and crucible are immersed. 1B - suitable substitute arrangement for 1A where more desirable electrical balance is unavailable.

Figure 2 - Apparatus for vacuum impregnation of ground sample with kerosene. Crucible is placed in chamber which is drawn to vacuum capacity of pump. Valve in separating funnel which serves as the kerosene reservoir is opened slightly to allow kerosene to trickle into the crucible until completely covering the sample. Pumping continues until bubbling ceases in the crucible. Chamber is then bled back to atmospheric pressure via the air intake and the crucible returned to "C" as shown in Figure 1A and is weighed after sample impregnation.





after being filled to near-capacity with kerosene, and it is observed through the glass chamber to see that outgassing of the shale is complete (no bubbling is observed).

The sample is then brought back to atmospheric pressure, and the crucible is removed from the chamber and is returned to the sample pan (Figure 1). The laboratory jack is raised back to lock position and the original piece of weigh paper is replaced on the balance pan. The worker then records the weight of the sample immersed in kerosene, and the calculation of matrix density becomes simply a computation from weight differences.

In constructing the apparatus of Figure 1, attention should be given to four possible sources of error in order to make valid high-precision measurements. The physical components which may contribute to error are examined in the following discussion. The number of the paragraph heading corresponds to the labeled number on the schematic shown in Figure 1A.

1) The immersion pan must be supported by the thinnest possible wires. Changes in depth of the immersion pan between weighing in air and weighing in liquid will produce immersion of a different volume of supporting wire. On a sensitive balance, the weight change thus produced is measurable.

2) Samples of differing sizes, particularly bulk-density specimens, will cause different changes of the level of the fluid in the pan, and thus produce a change in the volume of immersed supporting wire. Narrow vessels tend to increase such changes in fluid level. Virtually all publications which illustrate immersion methods show an unsuitably narrow vessel such as a beaker (see for example 1B) to contain the fluid. Changes of fluid level can be greatly attenuated by substituting a large, wide pan to contain the fluid instead of the narrow vessel.

3) The use of a suitable fluid of a known, precisely calibrated specific gravity is essential. Virtually all published procedures suggest calibrating such fluids through use of a reference fluid (usually water) in pycnometer. In addition to the replicate runs which are required to initially standardize the fluid, the accuracy of such methods in rooms which are not temperature-controlled is highly questionable. Normally, the fluid will have to be re-standardized every hour or two because of fluid changes produced by variations in temperature or, in the case of certain organic liquids, by evaporation. The problem is overcome by use of a single piece of rock crystal quartz which is essentially free of visible defects or inclusions. We utilize a 27 g piece of clear Brazilian quartz which is assumed to have a true density of 2.654 g/cc. It is simply weighed before and after immersion and the unknown specific gravity of

the fluid is calculated from the quartz standard. The same piece of quartz is used to calibrate the fluid for both bulk density and matrix density, hence very consistent measurements are obtained because all samples are referenced to a single standard.

The immersion fluid utilized in published procedures has been mercury (Clemency, 1972), water (Shapiro, 1975), light oil (Brownell, 1977, p. 3) and kerosene (this paper). Our choice of kerosene for an immersion liquid is based upon its low surface tension, its tendency not to trap air bubbles on the specimen, its low rate of evaporation, its comparative non-reactivity with shales, and its safe handling properties. Water contact with shale is to be avoided where possible. The reaction of water with Devonian shales to produce swelling, slaking, and secondary sulfate salts such as copiapite and halotrichite-pickeringite is visible in black shale outcrops. Also a number of sulfates in minor amounts are persistently seen in X-ray diffractograms taken from core samples. Shales exposed to kerosene do not swell even when immersed for long periods of time. The use of mercury, toluene, and carbon tetrachloride for immersion fluids as suggested in several references is a needless health hazard.

4) The necessity of keeping the depth of immersion of the specimen-holder consistent between weighing in air and weighing in fluid demands that the pan of fluid be returned to precisely the same point for each weighing. For this purpose we utilize a laboratory jack with a mechanical stop.

By minimizing error at these four sources, the apparatus allows one to make use of the extended precision provided by the high-precision balance. The balance utilized should be capable of measuring weight differences of relatively heavy specimens (20 grams or greater in the case of bulk-density specimens) within one milligram precision. Sufficient precision cannot be obtained with either a Jolly balance or triple-beam balance.

Requirements of precision are fulfilled by the better top-loading electric balances (this paper) and the older style double-pan analytical balance such as shown in Figure 1B (ASTM, 1976, pt. 15, p. 797-799).

Sample calculation of matrix density from vacuum crucible methods:

a) Calibration of fluid

Standard: Brazilian Quartz; density = . . . . . 2.654 g/cc  
Weight of standard in air = . . . . . 27.199 g  
Weight of standard in fluid = . . . . . 18.903 g  
Weight of displaced fluid = . . . . . 8.296 g  
Volume of standard = volume of displaced fluid = . . 10.248 cc  
Density of fluid = . . . . . 0.8095 g/cc

b) Measurement of sample matrix density

Density of fluid = . . . . . 0.8095 g/cc  
Weight of sample in air (balance zeroed with  
immersion pan in fluid) = . . . . . 0.568 g  
Weight of sample in fluid after vacuum impregna-  
tion with fluid = . . . . . 0.399 g  
Volume of sample from weight loss (.568-.399)g/  
.8095g/cc = . . . . . .209 cc  
Matrix density = . . . . . 2.72 g/cc

A number of alternate methods by which to obtain the density of powders or fine particulates were reviewed. Methods used commonly for determination of rock or rock-like materials such as refractory brick or ceramic ware (ASTM, 1976, pt. 17, p. 77-78; ASTM, 1976, pt. 15, p. 24-26) were considered to be too imprecise for use in measurement of grain density of shales.

The pycnometer method (ASTM D 153-54; 1976, pt. 28, p. 53-61) has been used on deep sea sediments (Hamilton, 1976) and on Devonian shales (Kalyoncu and others, 1977). It is possible to produce replications within about  $\pm 0.01$  to  $\pm 0.02$  g/cc under carefully controlled conditions. However, meeting the requirements of precision is tedious, and the method is not attractive for making determinations on large numbers of samples.

Shapiro (1975, p. 71) provides procedures for the employment of heavy liquids to obtain powder densities. Such methods provide good approximations from very small amounts of sample, but the precision is only  $\pm 0.04$  g/cc. When used for porosity estimates in shales, this error would commute to  $\pm 1.5\%$  which is

not nearly precise enough for specimens whose total porosity may lie within that very range. Furthermore, heterogenous mixtures of minerals with individual densities which vary by more than 0.04 g/cc cannot be measured by this method, because the mineral powder may separate into one or two distinct layers in the liquid. The method of heavy liquids may perhaps be useful for a convenient check on anomalous values but is inadequate for routine measurement of matrix density of shales.

Commercial automatic pycnometers which employ iterative gas expansion or measurement of volume of powders by helium from a chamber of known volume are available, and under favorable conditions accuracy of measurement to within  $\pm 0.01$  g/cc is possible. The writers did not have access to one of these instruments to evaluate it. However, precision cited by the manufacturers indicates that these would be suitable substitutes for the apparatus in Figures 1 and 2 if several grams of sample are available.

## 2) Determination of bulk density by method of Archimedes

The calculation of bulk density is very simple when employing the immersion principle of Archimedes, and requires only a known fluid density and the weight of the object in air and in the fluid. The apparatus previously shown in Figure 1 is utilized. However, some sample preparation of the bulk density sample block is required.

The bulk-density block must absolutely be taken from the same vertical interval which serves as the source for the samples used for other studies with which comparisons are to be made. It is difficult to achieve reliable bulk-density determinations on uncoated shale specimens used for immersion methods. In order to provide stable weighings, the outer surfaces of the shale block must be sealed to prevent the immersion fluid from being drawn into tiny capillaries, pores, or fractures. For purposes of sealing, apply three light coats of aerosol Krylon lacquer onto the blocks. The weight addition of the lacquer is small, but measurable. The resulting error which will occur in density determinations is very small, and even this is approximately correctable, if necessary.

Percent error of any density measurement may be expressed by:

$$\% \text{ Error} = \frac{\rho_l - \rho_t}{\rho_t} \times 100$$

where:  $\rho_l$  is the measured density

$\rho_t$  is the true density

The numerical true density of a solid may be obtained by dividing its mass in grams by its volume in cubic centimeters. If we assume that the solid is in the shape of a true sphere of radius  $r$  and weight  $w$  then its volume ( $V$ ) is given by:

$$V = 4/3 \pi r^3$$

and  $\rho_t = W/V$

Now, assume the sphere is coated uniformly with a layer of Krylon of thickness  $m$ . The volume  $V_1$  of the coated sphere is then given by:

$$V_1 = 4/3 \pi (r + m)^3$$

The volume ( $V_k$ ) of the Krylon comprising the coating is computed from a volume difference between two spheres expressed as:

$$\begin{aligned} V_k &= 4\pi \int_r^{r+m} x^2 dx \\ &= 4/3 \pi (r + m)^3 - 4/3 \pi r^3 \end{aligned}$$

The density ( $\rho_1$ ) of the coated sphere will be a function of the decimal fraction of its volume as occupied by Krylon of density  $\rho_k$ , and by its volume as occupied by the substance of density  $\rho_t$ . Therefore:

$$\frac{V}{V_1} (\rho_t) + \frac{V_k}{V_1} (\rho_k) = \rho_1$$

By substitution:

$$\begin{aligned} \% \text{ Error} &= \frac{\rho_1 - \rho_t}{\rho_t} \times 100 \\ &= \frac{\frac{V}{V_1} (\rho_t) + \frac{V_k}{V_1} (\rho_k) - \rho_t}{\rho_t} \times 100 \\ &= \frac{[4/3 \pi r^3 / 4/3 \pi (r + m)^3] \rho_t + [(4/3 \pi (r + m)^3 - 4/3 \pi r^3) / 4/3 \pi (r + m)^3] (\rho_k) - \rho_t}{\rho_t} \times 100 \end{aligned}$$

The above equation is easily evaluated numerically. From actual measurements, density of dry Krylon ( $\rho_k$ ) was derived as

1.1 g/cc. By spray coating glass spheres of known density, it was determined that three coats total 11 microns in thickness. Thus  $m = 0.0011$  cm. An assumed density of a perfect shale sphere of 2.70 g/cc for  $t$  is reasonable. When these numerical values are substituted into the above expression, it is reduced to:

$$\% \text{ Error} = \frac{59.2592 r^3 + 40.7407 (r + .0011)^3}{(r + .0011)^3} \times 100$$

For a sample of radius of 1 cm (11.310 grams)

Error would be about -0.2%

Reproducible results from day to day and operator to operator were established at slightly better than  $\pm 0.01$  g/cc for bulk densities. For most shale samples, this converts to an error of about 0.4%. Thus as long as bulk density samples of over about fifteen grams are utilized, the error introduced by Krylon may be ignored. Figure 5 illustrates the plot of results derived from the above mathematical arguments. The error produced by Krylon will always be negative as long as the material which is coated has a density greater than 1.1 g/cc.

#### Calculation of Porosity from Density Data

The relationship of density to porosity is rigorously defined by geometric arguments.

Mathematically this is expressed:

$$\% \phi = \frac{\rho_{ma} - \rho_b}{\rho_{ma} - \rho_f} \times 100$$

where

$\phi$  = porosity

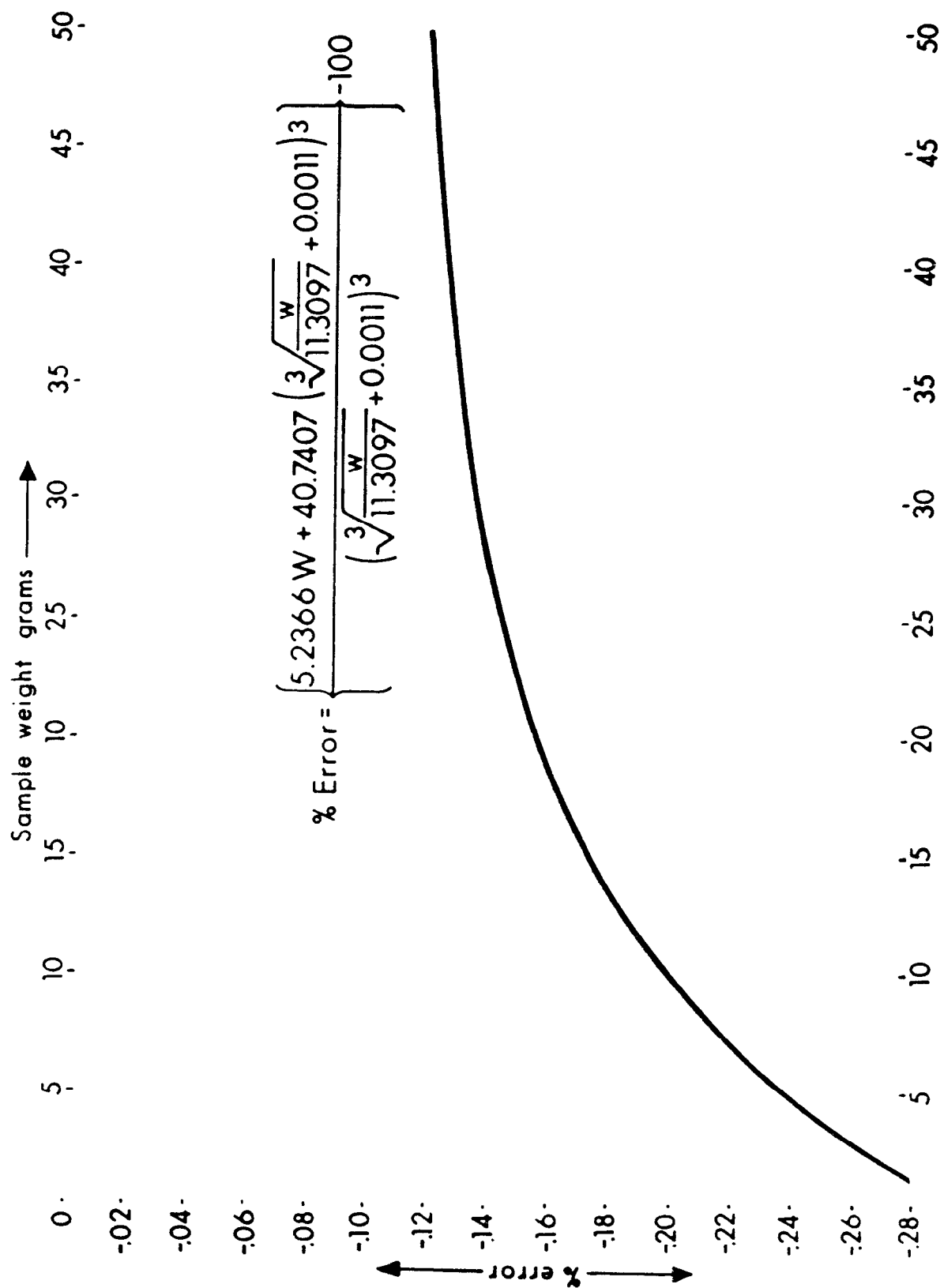
$\rho_{ma}$  = density of matrix

$\rho_b$  = bulk density

$\rho_f$  = fluid density of pore-filling fluids

In dry gas wells  $\rho_f$  is assumed to be zero.

Figure 3 - Nomograph for estimating approximate error in determination of bulk density caused by Krylon-coating of shales as function of sample weight. Spherical samples with density of 2.70 g/cc are assumed for construction of the curve.





## References Cited

- American Society for Testing Materials, 1976, Standard method of test for specific gravity of pigments: ASTM Std. Methods, D-153-54, pt. 28, p.53-61.
- American Society for Testing Materials, 1976, Standard method of test for specific gravity of semi-solid and solid bituminous materials by nickel crucible: ASTM Std. Methods, D-3289-74a, pt.15, p.797-799.
- American Society for Testing Materials, 1976, Standard method of test for specific gravity and absorption of fine aggregate: ASTM Std. Methods, C 128-73, pt.15, p.24-26.
- American Society for Testing Materials, 1976, Standard method of test for apparent porosity, water absorption, apparent specific gravity of fired whiteware products: ASTM Std. Methods, C-373, pt.17, p. 322-323.
- Brownell, W.E., 1977, Procedures for the characterization of Devonian shales: Proc. First Eastern Gas Shales Symp. U.S. Dept. Energy, N.T.I.S., MERC/SP-77-5, p.659-666.
- Clemency, C.V., 1972, A simple apparatus for the rapid and accurate determination of bulk densities or volumes of rock or mineral fragments: Jour. Sed. Petrology, v.42, p.982-984.
- Hamilton, E.L., 1976, Variations of density and porosity with depth in deep-sea sediments: Jour. Sed. Petrology, v.46, p.280-300.
- Kalyoncu, R.S., and others, 1977, Characterization and analysis of Devonian shales: Proc. First Eastern Gas Shales Symp. U.S. Dept. Energy, N.T.I.S., MERC/SP-77-5, p. 230-258.
- Shapiro, L., 1975, Rapid analysis of silicate, carbonate, and phosphate rocks - revised edition: U.S. Geol. Survey Bull. 1401, 76p.

## PREPARATION OF MEMBRANE-FILTER MOUNTS FOR

### X-RAY DIFFRACTION

E. B. Nuhfer

This is an inexpensive modification of the silver-membrane filter mount first described by Tucholke (1974). The procedure given here was devised by the writer about four years ago for analysis of sediment-trap samples. Primary advantages are excellent reproducibility, small sample consumption (20mg), good orientation of platy minerals, and rapid preparation. Disadvantages include dissolution of water-soluble minerals and production of synthetic sulfates by pyrite decomposition. Cubitt (1975) noted that the pressed pellet technique (first described by Fenner and Hartung, 1969), the smear technique (Gibbs, 1968), and the membrane-filter mount were sample preparation methods suitable for the quantitative comparisons of mineral content of shales.

The procedure developed by the writer follows:

- 1) If sample is high in organic matter (greater than 10% by weight loss on ignition after heating at 550C) the organic matter should be removed by low-temperature-ashing. A less desirable method of removal is to treat the sample for five days in concentrated hydrogen peroxide solution.

- 2) After the vial of ground sample (see paper by Renton in this book) has been thoroughly homogenized by tumble-mixing, 20mg of dry rock powder is placed in the bottom of a beaker and 150ml of distilled water are added. The beaker is placed into an ultrasonic bath for 15-20 seconds to insure sample dispersal, then the suspension is stirred on a mag-mixer for one minute. If this procedure is used for recent muds or suspended sediment where spex-mill grinding is not required, 22mg of dry sample may be weighed into a small agate mortar and hand-ground with moderate pressure for 100 strokes of the pestle. To insure good comparisons, the same worker should prepare all of the samples with the same number of grinding strokes. The sample is then scraped from the mortar onto a piece of weigh-paper atop the balance until the desired 20mg are registered, then the powder is dispersed as described above.

- 3) The apparatus used for filter-mounting is shown in Figure 1 and employs the Millipore filter holder and 25mm filters with 0.45 micron pores. To accommodate the small 25mm diameter filter, a gasket is required and is made from parchment paper used in packing the 47mm diameter filter for which the holder is

designed. A clean 23mm diameter hole is cut in the center of the parchment with a laboratory cork-cutter; the gasket is soaked in water before mounting onto the holder for use. The filter is placed onto the gasket and soaked with distilled water from a wash-bottle after which the vacuum is drawn to seal the filter over the opening in the parchment gasket.

4) With vacuum being drawn onto the filter holder, remove the beaker from the mag-mixer and pour all of the suspension immediately into the holder. After the fluid has been drawn through the filter, allow the vacuum to draw for an additional minute. Then, turn off the vacuum and cover the filter mount gently with four or five paper towels until dry. After drying, the samples should be relatively flat, but can be flattened completely by placing the filters sediment-side-up on a paper towel and covering with a clean piece of plate glass. When dry, these sample mounts make excellent color comparators for use with Munsell or standard Geological Society of America Color charts.

5) To mount the sample into the diffractometer, a piece of double-sticky tape is placed on a glass slide or onto the manufacturer's mounting plate and the filter is affixed to it with a flat spatula. Excess filter which may overhang the edges must be trimmed away with a new razor blade.

For maintaining precision, this method utilizes the same sample weight spread over the same area of filter by the same vacuum pressure, and thus results in a very good quality X-ray diffraction sample. 20mg of sample was determined as the optimum weight for use with the 25mm diameter filters. This is double the amount required for producibility and slightly less than the amount which will produce a sample coating of sufficient thickness to begin to cause problems by chipping and peeling. If peeling does occur, the filter can be placed into a beaker of water in an ultrasonic bath, the sample re-dispersed and remounted. The 25mm filters provide just enough area to cover the X-ray beam which is generated by most instruments, and therefore optimum use of sample and materials results from their employment. The larger 46mm filters which are designed for the holder may be used, but require 70mg of sample to maintain the recommended weight-per-unit area.

Comparative standards of "knowns" may be blended in various weight proportions during the step of dispersion in the ultrasonic cleaner. However, use of high-density orienting internal standards such as  $\text{MoS}_2$  (see Cody and Thompson, 1976) is not possible because the specific gravity of the standard causes it to preferentially settle onto the filter ahead of the sediment.

The problems of absolute quantification of clay-mineral phases are well known (see Devine, Ferrell, and Billings, 1972)

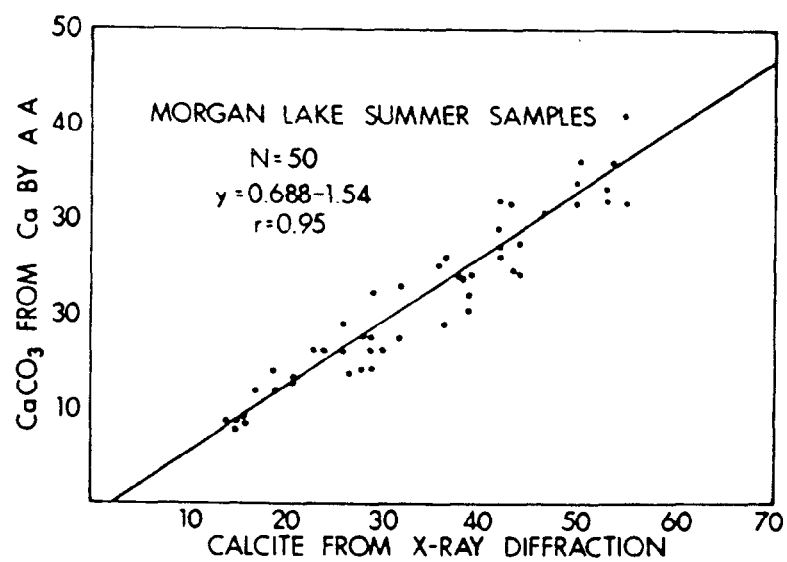
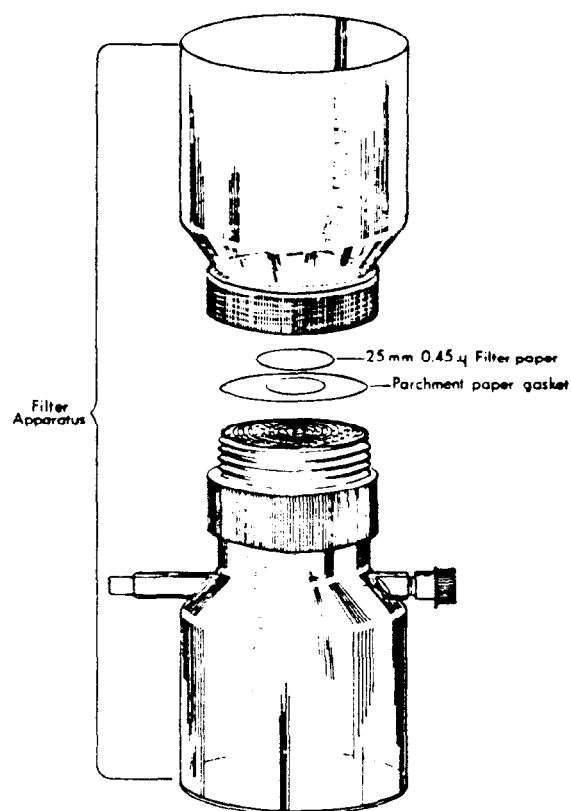
and may perhaps never be resolved through X-ray diffraction. Some recent workers have suggested utilizing chemical analyses of fine-grained sediments to derive normative percentages of minerals (Sonerholm, 1975). Such procedures can be justified only if X-ray-amorphous mineraloids are absent. The work of this writer has shown that recent muds and suspended sediments contain significant amounts of amorphous silicates, oxides, sulfates, and organic-related complexes. The calculation of mineral percentages from chemical analyses is indefensible in such samples. The stage of diagenesis when amorphous mineraloids become unimportant (if in fact such a stage even exists for fine-grained clastics!) has never been deduced, nor have researchers addressed themselves to the difficult task of discovering how much of a Paleozoic shale is comprised of amorphous matter. Thus, while clay minerals may be identified (Lucas, 1968; Carroll, 1970) and good relative quantification be made for comparative purposes, absolute quantification yet leaves much to be desired in fine-grained rocks and sediments.

The success of mineral quantification utilizing X-ray diffraction of membrane filter-mounts is illustrated in Figure 2. The linearity provided here is probably the best which can be expected from earth materials routinely analysed with conventional diffractometers. Of interest is the slope of the best-fit line in Figure 2 which shows blatantly that the absolute amount of calcite which results from calculations from uncorrected data (Renton, 1977) is a gross overestimate of the amount of calcite actually present. Such low linear slopes are not observed in similarly derived cross-plots of coarse-grained ancient rocks (see Renton, 1977). The complex nature of shales makes derivation of such cross-plots difficult because an absolute quantification of a single mineral cannot be obtained from either chemical analysis or point-counting of thin sections with sufficient accuracy to merit developing of a working curve.

The work on the Eastern Gas Shales Project has resulted in diffraction studies and thin-section studies of over 400 correlative shale samples, and correlations between minerals quantified by point-counts and minerals quantified by X-ray diffraction are consistently low. These results are in accord with the observations of Halley (1978) and show that thin-section point-counting is a very unreliable method for quantification of minerals in fine-grained clastic materials. X-ray diffraction, in spite of inherent problems, appears to be a precise, if not accurate, method for quantification of minerals in fine-grained clastic sediments.

Figure 1 - Millipore filter apparatus utilized to prepare  
membrane filter mounts of sample for color comparison and  
X-ray diffraction

Figure 2 - Plot of X-ray derived calcite versus calcite  
calculated from total calcium in sample as determined by  
atomic absorption analysis. Samples are summer samples  
of suspended sediment from Morgan Lake, New Mexico



#### References Cited

- Carroll, D., 1970, Clay minerals: a guide to their X-ray identification: Geol. Soc. America Spec. Paper 126, 75p.
- Cody, R.D., and Thompson, G.L., 1976, Quantitative X-ray diffraction analyses of clays using an orienting internal standard and pressed disks of bulk shale samples: *Clays and Clay Minerals*, v.24, p.224-231.
- Cubitt, J.M., 1975, A regression technique for the analysis of shales by X-ray diffractometry: *Jour. Sed. Petrology*, v.45, p.546-553.
- Devine, S.B., Ferrell, R.E., and Billings, G.K., 1972, A quantitative X-ray diffraction technique applied to fine-grained sediments of the deep Gulf of Mexico: *Jour. Sed. Petrology*, v.42, p. 468-475.
- Fenner, P., and Hartung, J.R., 1969, Laboratory processing of halloysite: *Clays and Clay Minerals*, v.17, p.42-45.
- Gibbs, R.J., 1968, Clay mounting techniques for X-ray diffraction analysis: *Jour. Sed. Petrology*, v.38, p.242-244.
- Halley, R.B., 1978, Estimating pore and cement volumes in thin section: *Jour. Sed. Petrology*, v.48, p.642-650.
- Lucas, J., 1962, Transformation of clay minerals during sedimentation, study on Triassic clays: Reports of the Geol. Map Service Alsace Lorraine, n.23; English translation 1968, Israel Program for Scientific Translations, Springfield, Va., U.S. Dept. Commerce Clearinghouse for Federal Scientific and Tech. Information, 203p.
- Renton, J.J., 1977, Use of uncorrected X-ray diffraction data in quantitative analytical determinations: U.S. Dept. Energy, N.T.I.S., MERC/C-77/10, 20p.
- Sonerholm, P.A., 1975, Normative mineral distributions in Utah Lake sediments; a statistical analysis: *Brigham Young University Geology Studies*, v.21, p. 97-118.
- Tucholke, B.E., 1974, Determination of montmorillonite in small samples and implications for suspended-matter studies: *Jour. Sed. Petrology*, v.44, p. 254-257.

## CHEMICAL ANALYSIS OF FINE-GRAINED CLASTICS

### USING $\text{LiBO}_2$ -HCl-HF DISSOLUTIONS

E. B. Nuhfer and R. R. Romanosky

This scheme was used for interlaboratory comparison of U.S.G.S. Standard SD01 earlier in the Eastern Gas Shales Project and to prepare secondary standard working curves for analysis of Devonian shales by X-ray fluorescence. It is suitable for laboratories with modest facilities which are limited for processing of large numbers of samples. In general, most institutions provide one or more of the following facilities: colorimetry, atomic absorption spectrophotometry, flame photometry, emission spectroscopy, sometimes X-ray fluorescence, and more rarely polarography and inductively coupled plasma torch spectroscopy.

Possibly because of bias through their own experience, the writers prefer dissolution schemes for sample preparation. Dissolution aids in overcoming many matrix problems and is adaptable to a wide variety of analytical methods.

a) Preparation of ash - The procedure of Dean (1974) is used to determine organic matter by LOI between  $100^\circ$  and  $550^\circ$  and then further LOI (mainly due to evolution of  $\text{CO}_2$  from carbonates and sulfur from sulfides) between  $550^\circ$  and  $1000^\circ\text{C}$ . On small amounts of sample (less than 0.1 g) inert metal crucibles are preferable to ceramic ones because they do not absorb any atmospheric humidity. The problem of small sample size did not occur in the shale analyses. However, the scheme successfully handled samples of sediment-trap materials of less than 20 mg.

b) Dissolution of ash (sample requirement 10 mg, preferably 100 mg) - The given dissolution process utilized the lithium metaborate flux originally suggested by M. L. Keith (Suhr and Ingamella, 1966, p. 734). A number of flux-fusion dissolution procedures (Abbey, Lee and Bouvier, 1974; Medlin, Suhr, and Bodkin, 1969; Shapiro, 1975) have been published. While the general process described by these writers are satisfactory, minimum transfer of materials between containers, thorough homogenization of flux and sample, and depolymerization of silica by minimal addition of fluoride ion (Nuhfer and Seckel, 1977) are all essential for efficiency and precision when handling large numbers of very small samples. The procedure is as follows:

1) Weigh 0.500 g of lithium metaborate ( $\text{LiBO}_2$ ) into clean 1-dram plug-type glass vials (Figure 1). Avoid use of weigh paper in transfer of small amounts of sample from balance to vial. Add 100 mg of the dry ash directly to each vial. Hand shake



vigorously for two minutes or tumble mix all vials simultaneously for a period of four hours (Figure 2).

2) Tap contents of each vial into a clean graphite crucible. Stack the crucibles in a small muffle furnace (Figure 3) while recording a map of where each sample is placed. Fuse at 1000°C for one hour. Do not permit furnace to rise beyond 1050°C. If the furnace rises into the range near 1150°, lead loss from the sample will occur and phosphorous from the furnace liner may vaporize and become entrained in the sample. Fuse also 0.500 g of  $\text{LiBO}_2$  for a blank and carry through the procedure.

3) Add 25 ml of 4M HCl to each of 125ml widemouth LPE bottles (Figure 4). At the end of time allotted for fusion, use asbestos gloves and tongs to withdraw a hot crucible, gently swirl so as to allow the molten bead to touch and assimilate any sample material adhering to the inside of crucible, and pour the molten material into the pool of acid in the LPE bottle; then cap (Figure 5). Label the bottle and cross out sample from the previously prepared map. Do not permit furnace to cool below 850 C. Pouring of molten beads from crucibles circumvents the difficulty of removing stuck glass beads, prevents loss of sample, and without violence effectively shatters the beads to promote dissolution. Continue until all beads are shattered in the bottles. Add 50ml of distilled-deionized water to each bottle and shake.

4) Using a calibrated dropper bottle or Eppendorf pipet (wear protective gloves and goggles) add 1 ml of concentrated HF to each bottle (Figure 6). Shake bottles every two hours and allow to stand for at least 8 hours. If white flecs of silica yet are visible in the solution at the end of that time, add another 0.5 ml of HF. Shake 4 times daily and allow to stand for another day. Do not add excess HF to hasten dissolution - this can result in precipitation of less soluble fluorides or loss of silica by volatile tetrafluoride. By utilizing the above proportions, the writers have never observed either fluoride precipitation or silica loss in analysis of any earth material.

5) Use a good grade of filter paper, an LPE volumetric flask, and LPE funnel. Line funnel with paper, moisten with pure distilled water, and pour solution through the paper-lined funnel into the flask. Add a small amount of distilled water to the bottle, shake, and pour through the funnel. With a wash bottle rinse down the filter paper until the mark on the volumetric flask is reached. Usually, 100 mg samples are brought to volume of 125 ml. If samples are consistently smaller than 100 mg, the worker may wish to fuse 20 mg of sample in 0.500 g of  $\text{LiBO}_2$ , then bring to final volume of 100 ml. Rinse and shake the bottle thoroughly to remove any remaining flecs of graphite. These will

clog nebulizers and aspirators of AA units and flame photometers unless completely removed. Shake bottle dry and pour contents of volumetric flask back into bottle. Rinse flask, wash filter paper with more water, and proceed to next sample. Samples are now at volume and ready to run. Shelf life of the final solution has proven to be over one year and perhaps is unlimited. Use of nitric acid in place of hydrochloric may speed dissolution but will desensitize atomic absorption determination of iron and manganese.

c) Analysis of whole rock from final solution - For general colimetric determinations on the final solution, the reader is referred to Shapiro (1975) and Ingamells (1966). In routine analysis, the writers utilize an unpublished phosphorous determination method developed by John Husler of the University of New Mexico (1976, personal communication) and the silica method published by Shapiro (1975, p. 46-47). Husler's method is as follows:

1) To 180 ml of 5%  $\text{H}_2\text{SO}_4$  in a plastic bottle, add 36 ml of 8%  $\text{NH}_4\text{MoO}_4$  (4 g  $\text{NH}_4$  into 50 ml  $\text{H}_2\text{O}$ ). Then add 36 ml of a solution containing 10% ascorbic acid and 3% NaF (1.2 NaF plus 4 g ascorbic acid into 40 ml  $\text{H}_2\text{O}$ ). The final solution is termed Husler's Reagent by the writer.

2) Use a volumetric pipet and transfer equal amounts of the AA solution and Husler's Reagent into a plastic beaker. The actual amount required depends on the cell utilized in the colimeter. The arrangement in Figure 7 requires only 500  $\mu\text{l}$  of each.

3) Place beakers in a warm water bath (about  $80^\circ\text{C}$ ) and heat for at least 20 minutes.

4) Samples are removed individually from the water bath and run on a colimeter set at 700 nm (or a 670 nm color filter is acceptable). The colorimeter is zeroed using the blank AA solution.

5) Standards are run to prepare working curves.

Twelve other elements are run routinely by atomic absorption using the conditions shown in Table 1. Alternately, differential pulse anodic stripping voltammetry and inductivity coupled plasma torch (see Greenfield, 1977) have proven to perform analyses well on the final solution. In the former, a plastic cell must be utilized. Also the glass of the mercury electrode must be protected with shrinkable tubing to prevent leaching of lead from the glass during analysis, which produces growth of lead peaks on the replicate runs (Romansky and Nuhfer, in preparation).

Pb, Cr, Ni, Co and several other trace materials have proven to be satisfactorily determined on the final solution utilizing flameless atomic absorption (Nuhfer and Romanosky, 1979) following conditions of the instrument manufacturer. Owens and Gladney (1976) list conditions for determination of 11 trace elements on  $\text{LiBO}_2$  flux-fusion dissolutions by flameless atomic absorption.

If elements such as arsenic and cadmium (which may be lost by volatilization at fusion temperatures) are sought, low temperature dissolution in teflon-lined vessels (Bernas, 1968; Buckley and Cranston, 1971; Rantala and Loring, 1975) is recommended over the more rapid flux-fusion method.

Multi-element standards are prepared from standard rock samples processed in a method identical to that of the unknown. Abbey (1977) provides the most complete summary of compositions of standards and addresses from which these standards may be obtained.

Spiking of blank solution with commercially prepared standard solutions also yields suitable standards. The high calcium values of some samples may exceed available whole-rock standards samples. For such cases, fusion of reagent grade  $\text{CaCO}_3$  which has been freshly ignited at  $1000^\circ\text{C}$  is recommended. Prepare ten standards by  $\text{LiBO}_2$  fusion using  $1000^\circ\text{C}$   $\text{CaCO}_3$  ash enriched successively in 10 mg increments. Generally, dilution to 100-fold of sample and standards is required on AA analysis of rock dissolutions to achieve satisfactory results without addition of lanthanum salts.

For establishing geochemical relationships of variables such as mineralogy and organic content between samples, the writer suggests that the researcher should record the elemental data from the ash, the LOI at  $550^\circ\text{C}$ , and the LOI at  $1000^\circ\text{C}$  "as is" and not attempt to utilize calculated compositions of whole-sample for numerical analyses. This is because real changes which are clearly discernible in the ash analyses may be obscured by dilution with organic matter when reported in terms of whole-sample composition.

The same obscure results will, of course, be yielded if the researcher fuses or digests whole-sample rather than ash, with the probable additional consequence that concentrations of some materials will be diluted beyond detectable limits. Furthermore, evaluation of the quality of the total analyses by inspection of how nearly all measured components sum to 100% will not be possible (see Nuhfer and Renton, 1979).

ELEMENT	WAVELENGTH (nm)	SLIT SETTING (nm)	OXIDANT	BURNER HEAD ORIENTATION
Al	394.4	0.7	Nitrous oxide	0°
(*) Ca	422.7	1.4	Nitrous oxide	90°
Cu	324.8	0.7	Air	0°
Fe	386.0	0.2	Air	0°
* K	769.9	1.4	Air	45°
Mg	285.2	0.7	Nitrous oxide	90°
Mn	279.5	0.2	Air	0°
Na	589.6	1.4	Air	90°
Si	250.7	0.7	Nitrous oxide	0°
Sr	460.7	1.4	Nitrous oxide	0°
Ti	365.4	0.2	Nitrous oxide	0°
Zn	213.9	0.7	Air	0°

\* Flame Emission

(\*) Alternate Method - Flame Emission

Table 1 Instrument conditions for atomic absorption/flame emission analysis of solutions prepared from LiBO<sub>2</sub> flux-fusion rock dissolutions as described in text. Fuel-oxidant mixtures are adjusted for maximum absorption.

Figures 1-6. Processing steps in sample preparation by flux-fusion dissolution.

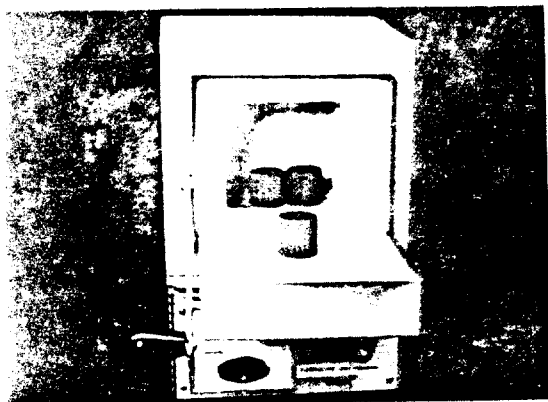
- 1) All weighings of sample and flux are done within 1-dram vials so as to eliminate transfers of sample on weigh-paper.
- 2) The 1-dram vials serve as containers during 4 hours of tumble-mixing which assures the mixing of flux and sample.
- 3) The samples are tapped from vials into graphite crucibles and are fused for one hour at 1000 C. Small muffle furnaces permit easy extraction of crucibles yet permits simultaneous fusion of up to 30 samples stacked in tiers.
- 4) While samples are fusing, 25ml of 3.7M HCl are pipetted into 125 ml LPE bottles. Automatic dispenser shown permits rapid and accurate dispensing of acid.
- 5) Hot crucible is withdrawn from furnace, swirled to allow molten bead to sweep up material adhering to the sides and the molten bead is poured into acid in the LPE bottle. The empty part of the bottle acts as a chimney above the acid pool and prevents loss of sample through spattering. After beads are in bottles, 50 ml of pure distilled de-ionized water are added to each bottle by means of a dispenser as shown at 4.
- 6) After 4 hours, 1 ml of concentrated reagent-grade HF is added via a calibrated dropper bottle to depolymerize silica. Samples are shaken twice daily and observed on the following day to make certain that the beads have completely dissolved. Samples are now ready to be filtered and brought to volume as described in text.



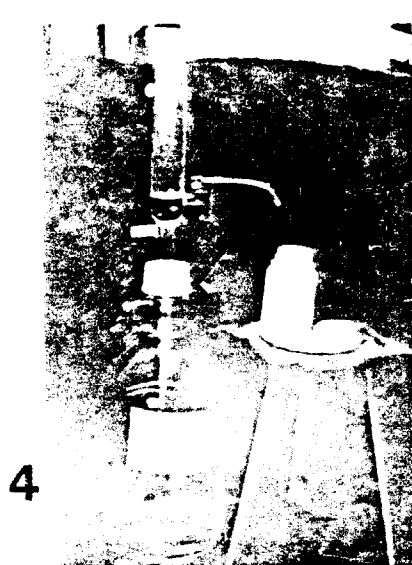
1



2



3



4



5



6

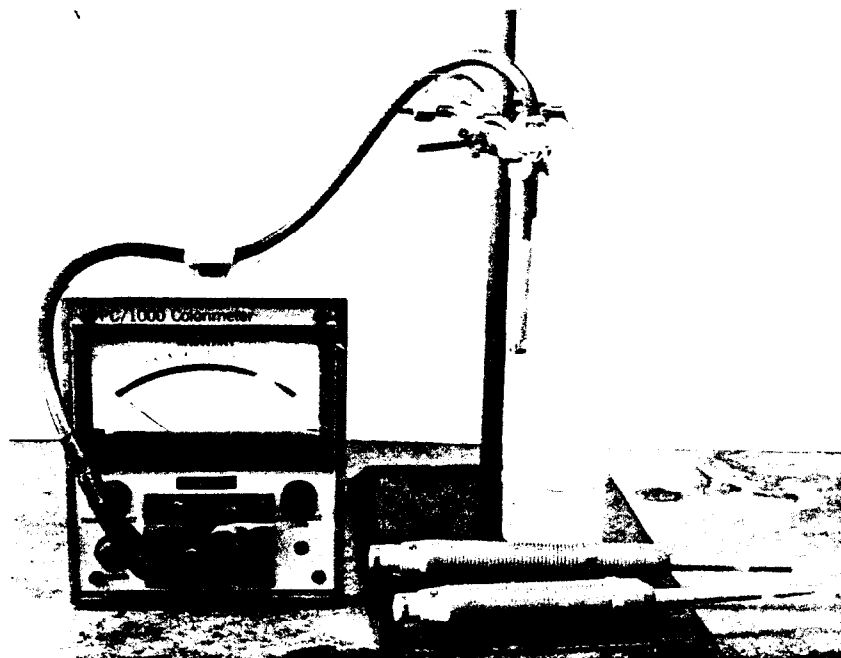


Figure 7. Colorimeter equipped with fiber-optics probe. This system is ideal for rapid analysis of flux-fusion dissolutions. Precise microcolorimetric work is made possible through employment of automatic pipettes such as those shown in the foreground. Consumption of sample dissolution and colorimetric reagents is minimized by use of the pipettes in conjunction with the small disposable plastic test tubes which permit colorimetric readings to be taken on small volumes of solution. Employment of the tubes attached to LPE dissolution containers by rubber bands as shown allows replications to be run on large numbers of samples without time-consuming labeling of separate containers for aliquots. Test tubes are inert to reagents used for dissolution.

#### References Cited

- Abbey, S., 1977, Studies in "standard samples" for use in the general analysis of silicate rocks and minerals - part 5: 1977 edition of "usable" values: Geol. Survey Canada, Paper 77-34, 31p.
- Abbey, S., Lee, N.J., and Bouvier, J.L., 1974, Analysis of rocks and minerals using an atomic absorption spectrophotometer: Geol. Survey Canada, Paper 74-19.
- Bernas, B., 1968, A new method for decomposition and comprehensive analysis of silicates by atomic absorption spectrometry: Analytical Chem., v.40, p. 1682-1686.
- Buckley, D.E., and Cranston, R.E., 1971, Atomic absorption analyses of 18 elements from a single decomposition of aluminosilicate: Chem. Geology, v.7, p.273-284.
- Dean, W.E., Jr., 1974, Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods: Jour. Sed. Petrology, v.44, p.242-248.
- Greenfield, S., 1977, The inductively coupled plasma torch - a source for all reasons: Spex Speaker, v.23, n.3, p.1-6.
- Ingamells, C.O., 1966, Absorptiometric methods in rapid silicate analysis: Analytical Chem., v.38, p.1228-1234.
- Medlin, J.H., Suhr, N.H., and Bodkin, J.B., 1969, Atomic absorption analysis of silicates employing LiBO<sub>2</sub> fusion: Atomic Abs. Newsletter, v.8, n.2, p. 25-29.
- Nuhfer, E.B., and Renton, J.J., 1979, Whole-rock vs. whole-ash analysis of sedimentary rocks - the elusive 100% summation: Atomic Abs. Newsletter, in review.
- Nuhfer, E.B., and Romanosky, R.R., 1979, Determination of lead in earth materials from lithium metaborate flux-fusion dissolutions: Atomic Abs. Newsletter, v.18, n.1, p.8-9.
- Nuhfer, E.B., and Seckel, J.A., 1977, An improved LiBO<sub>2</sub> flux-fusion sample preparation scheme for rapid analyses of earth materials (abs.): 9th Central Regional Meetings Program American Chem. Soc., p.91.
- Owens, J.W., and Gladney, E.S., 1976, Lithium metaborate fusion and the determination of trace metals in flyash by flameless atomic absorption: Atomic Abs. Newsletter, v.15, p. 95-97.



Rantala, R.T.T., and Loring, D.H., 1975, Multi-element analysis of silicate rocks and marine sediments by atomic absorption spectrophotometry: Atomic Abs. Newsletter, v.14, p.117-120.

Shapiro, L., 1975, Rapid analysis of silicate, carbonate, and phosphate rocks - revised edition: U.S. Geol. Survey Bull. 1401, 76p.

Suhr, N.H., and Ingamells, C.O., 1966, Solution technique for analysis of silicates: Analytical Chem. v.38, p.730-734.